

PATENT SPECIFICATION

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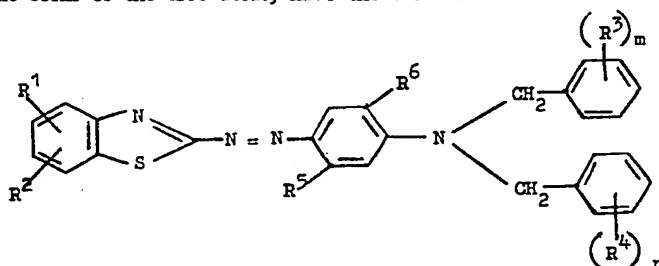
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(54) MONOAZO DYES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to monoazo dyes and their application to textile materials. According to the invention, there are provided water-soluble monoazo dyes which, in the form of the free acids, have the formula:



wherein each of R^1 and R^2 , independently, represents hydrogen, lower alkyl, cyano, halogen, lower alkoxy, nitro, thiocyno, sulpho, $-\text{SO}_2\text{R}^s$ wherein R^s denotes lower alkyl, $-\text{SO}_2\text{NR}^9\text{R}^{10}$ wherein R^9 and R^{10} independently denote hydrogen or lower alkyl or $-\text{COOR}^{11}$ wherein R^{11} denotes hydrogen or lower alkyl;

each of R^3 and R^4 , independently, represents hydrogen, halogen, nitro, alkyl, alkoxy or sulpho;

m and n have values of 1 or 2;

R^3 represents hydrogen, halogen, lower alkyl, lower alkoxy or acylamino; and

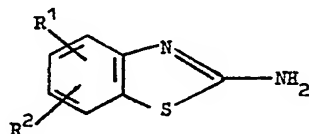
R^6 represents hydrogen, halogen, lower alkyl or lower alkoxy, with the proviso that only one of R^1 , R^2 , R^3 and R^4 is sulpho.

The expressions "lower alkyl" and "lower alkoxy" used herein mean alkyl and alkoxy groups containing one to four carbon atoms.

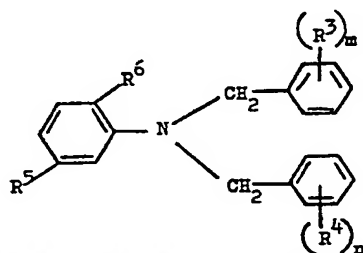
Acylamino groups which may be represented by R^6 include, in particular, groups of the formulae $-\text{NHCOQ}^1$ and $-\text{NH}\text{SO}_2\text{Q}^2$ wherein Q^1 represents hydrogen, alkyl (especially lower alkyl), aryl or aminoalkyl and Q^2 represents optionally substituted lower alkyl or aryl.

It is preferred that either R^1 or R^2 is sulpho.

The dyes of the invention may be prepared by diazotising a primary amine of the formula:



and coupling the resulting diazo compound with a tertiary amine of the formula:



wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , m and n have the meanings given above, the primary amine and the tertiary amine together containing only one sulphonic acid group.

Suitable primary amines for use in making the dyes include 2-amino-1,3-benzthiazole, 4-, 5-, 6- or 7-chloro-2-amino-1,3-benzthiazole, 4,6-dichloro- (or dibromo)-2-amino-1,3-benzthiazole, 6-methoxy-2-amino-1,3-benzthiazole, 6-thiocyano-2-amino-1,3-benzthiazole, 6-nitro-2-amino-1,3-benzthiazole, 6-cyano-2-amino-1,3-benzthiazole, 6-methylsulphonyl-2-amino-1,3-benzthiazole, 6-ethylsulphonyl-2-amino-1,3-benzthiazole, 2-amino-1,3-benzthiazole-6-sulphonic acid diethylamide, 2-amino-1,3-benzthiazole-6-sulphonic acid methylamide, 2-amino-1,3-benzthiazole-4-, 5-, 6- or 7-sulphonic acid, 6-chloro-2-amino-1,3-benzthiazole-4-, or 5-sulphonic acid, 6-methoxy-2-amino-1,3-benzthiazole-4- or 5-sulphonic acid and 6-methyl-2-amino-1,3-benzthiazole-4- or 5-sulphonic acid. The preferred diazo component is 2-amino-1,3-benzthiazole-5-sulphonic acid.

Examples of suitable coupling components include *N,N*-dibenzylaniline, *N,N*-dibenzyl-*m*-toluidine, *N,N*-dibenzyl-*m*-anisidine, *N,N*-dibenzyl-*m*-aminoacetanilide, *N,N*-dibenzyl-*m*-aminobenzanilide, *N,N*-dibenzyl-*m*-chloroaniline, *N,N*-dibenzyl-*m*-bromoaniline, *N,N*-di(*o*-, *m*- or *p*-chlorobenzyl)aniline, *N,N*-di(*o*-, *m*- or *p*-nitrobenzyl)aniline, *N,N*-di(*o*-, *m*- or *p*-methylbenzyl)aniline, *N,N*-di(*o*-, *m*- or *p*-methoxybenzyl)aniline and *N*-benzyl-*N*-(3-sulphobenzyl)aniline.

The reactions leading to the formation of the dyes of the invention may be performed using conditions that have been fully described in the prior art for such reactions. Similarly, the dyes may be isolated by known methods and, as in the case of other dyes containing sulphonic acid groups, it is often convenient to isolate and use the dyes in the form of their water-soluble salts, particularly their alkali metal or ammonium salts and especially sodium salts. It is to be understood that the invention relates to both the free acids and their salts.

The dyes of the invention are suitable for applying to polyamide textile materials such as wool and silk, but especially to synthetic polyamide textile materials, for example nylon 66, nylon 6 and nylon 11, using any of the general methods known for the application of acid dyes to such materials. The dyes provide orange to red shades having a high degree of fastness to wet treatments and to light.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

Example 1.

0.8 Part of sodium nitrite is dissolved in 10 parts of 98% sulphuric acid at 25—35°C and the solution is cooled to 0°C. 2.3 parts of 2-amino-1,3-benzthiazole-5-sulphonic acid are added with vigorous stirring and the temperature is maintained at 0°C during the addition of 12.5 parts of water. The mixture is stirred at 0°C for a further 2 hours after which the excess nitrous acid present is destroyed by the addition of sulphamic acid.

The diazonium salt suspension is then added, with stirring, to an ice cold mixture of 2.73 parts of finely divided *N,N*-dibenzylaniline and 100 parts of water and stirring is continued for a further 20 hours. The precipitated crystalline dyestuff, which is in the form of the free sulphonic acid, is collected by filtration, washed with water and converted to its sodium salt by treatment with sodium hydroxide. It dyes synthetic polyamide fibres or fabrics from a neutral or weakly acidic dyebath in clear red shades having good fastness to light and excellent fastness to wet treatments.

The 2-amino-1,3-benzthiazole-5-sulphonic acid used in this Example is prepared as follows:

24 Parts of 4-amino-3-nitrobenzene sulphonic acid sodium salt are dissolved in

125 parts of 1 molar sulphuric acid with stirring and the solution is cooled to 0°C and diazotised by the slow addition of 2 molar sodium nitrite solution. 15 Parts of sodium acetate are then added and the mixture is added to a stirred solution of 15.2 parts of ammonium thiocyanate and 0.5 part of cuprous thiocyanate dissolved in 200 parts of water. After 2 hours the evolution of nitrogen has ceased and no diazonium salt can be detected in the reaction mixture. The whole mixture is then added to a mixture of 50 parts of iron filings, 100 parts of water and 1 part of 36% hydrochloric acid which has previously been stirred and heated at 95°C for 30 minutes, and stirring at 90—95°C is continued for 2 hours. The mixture is then made alkaline by the addition of 4 parts of sodium carbonate and filtered. The clear filtrates are acidified by the addition of hydrochloric acid and the precipitate thus formed is collected by filtration, washed with water and dried at 120°C.

Example 2.

The N,N-dibenzylaniline used in Example 1 is replaced by 2.87 parts of N,N-dibenzyl-*m*-toluidine whereupon a dyestuff is obtained which dyes synthetic polyamide fibres or fabrics in bluish-red shades of similar high fastness.

If, in Example 1, the diazo and coupling components are replaced by the compounds indicated in the table, further dyestuffs which dye polyamide in orange to red shades are obtained.

Ex.	Diazo Component	Coupling Component
3	2-amino-1,3-benzthiazole-5-sulphonic acid	N,N-dibenzyl- <i>m</i> -anisidine N,N-dibenzyl- <i>m</i> -aminobenzanilide
4	„	N,N-dibenzyl- <i>m</i> -aminobenzanilide
5	„	N,N-dibenzyl- <i>m</i> -chloroaniline
6	„	N,N-dibenzyl-2-methoxy-5-methyl-aniline
7	„	N,N-dibenzyl-2-methoxy-5-acetyl-aminobenzaniline
8	2-amino-1,3-benzthiazole-6-sulphonic acid	N,N-dibenzylaniline
9	„	N,N-dibenzyl- <i>m</i> -toluidine
10	„	N,N-dibenzyl- <i>m</i> -aminobenzanilide
11	2-amino-6-chloro-1,3-benzthiazole-5-sulphonic acid	N,N-dibenzyl- <i>m</i> -toluidine
12	2-amino-6-methoxy-1,3-benzthiazole-5-sulphonic acid	N,N-dibenzyl- <i>m</i> -toluidine
13	2-amino-6-thiocyano-1,3-benzthiazole-5-sulphonic acid	N,N-dibenzyl- <i>m</i> -toluidine
14	2-amino-1,3-benzthiazole	3-(N-benzyl-N-3-methylphenyl-aminomethyl)-benzene sulphonic acid
15	2-amino-6-chloro-1,3-benzthiazole	„
16	2-amino-6-bromo-1,3-benzthiazole	„
17	2-amino-6-methyl-1,3-benzthiazole	„
18	2-amino-6-methoxy-1,3-benzthiazole	„
19	2-amino-6-cyano-1,3-benzthiazole	„
20	2-amino-6-thiocyano-1,3-benzthiazole	„
21	2-amino-6-methylsulphonyl-1,3-benzthiazole	„
22	2-amino-6-(N,N-dimethylsulphamoyl)-1,3-benzthiazole	„
23	2-amino-6-nitro-1,3-benzthiazole	„
24	2-amino-4,6-dichloro-1,3-benzthiazole	„

Ex.	Diazo Component	Coupling Component
25	2-amino-1,3-benzthiazole-5-sulphonic acid	N,N-bis(2-chlorophenylmethyl)aniline
26	..	N,N-bis(2-chlorophenylmethyl)- <i>m</i> -toluidine
27	..	N,N-bis(4-chlorophenylmethyl)- <i>m</i> -toluidine
28	..	N,N-bis(4-methylphenylmethyl)- <i>m</i> -toluidine
29	2-amino-5-(N,N-dimethylsulphamoyl)-1,3-benzthiazole	3-(N-benzyl-N-3-methylphenylaminomethyl)benzene sulphonic acid

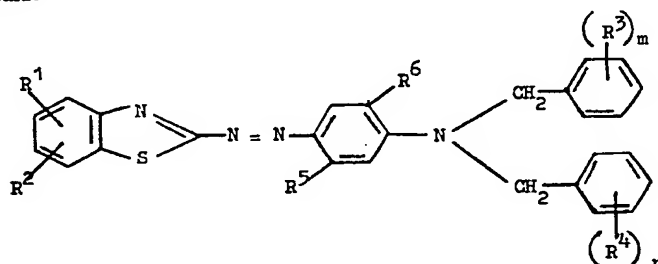
The 3-(N-benzyl-N-3-methylphenylaminomethyl)benzene sulphonic acid used in some of the Examples is obtained by the reaction of benzyl chloride with 3-(N-3-methylphenylaminomethyl)benzene sulphonic acid which is itself obtained by sulphonation of N-benzyl-*m*-toluidine.

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WHAT WE CLAIM IS:—

1. A water-soluble monoazo dye which, in the form of the free acid, has the formula:—

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wherein each of R¹ and R², independently, represents hydrogen, lower alkyl, cyano, halogen, lower alkoxy, nitro, thiocyno, sulfo, —SO₂R⁸ wherein R⁸ denotes lower alkyl, —SO₂NR⁹R¹⁰ wherein R⁹ and R¹⁰ independently denote hydrogen or lower alkyl or —COOR¹¹ wherein R¹¹ denotes hydrogen or lower alkyl;

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each of R³ and R⁴, independently, represents hydrogen, halogen, nitro, alkyl, alkoxy or sulfo;

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m and n have values of 1 or 2;

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R⁵ represents hydrogen, halogen, lower alkyl, lower alkoxy or acylamino; and R⁶ represents hydrogen, halogen, lower alkyl or lower alkoxy, with the proviso that only one of R¹, R², R³ and R⁴ is sulfo, the expressions "lower alkyl" and "lower alkoxy" meaning alkyl and alkoxy groups containing one to four carbon atoms.

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2. A water-soluble monoazo dye as claimed in claim 1 wherein R¹ and R² is sulfo.

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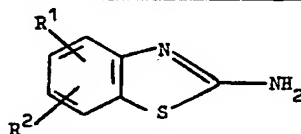
3. A water-soluble monoazo dye as claimed in claim 1 and specifically identified in Example 1 or Example 2.

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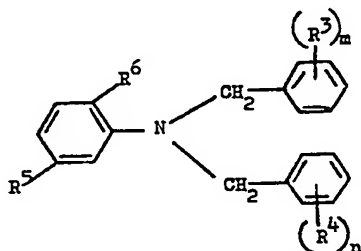
4. A water-soluble monoazo dye as claimed in claim 1 and specifically identified in any one of Examples 3 to 29.

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5. A method for the preparation of a water-soluble monoazo dye as defined in claim 1 which comprises diazotising a primary amine of the formula:



and coupling the resulting diazo compound with a tertiary amine of the formula:



wherein R¹, R², R³, R⁴, R⁵, R⁶, m and n have the meanings given in claim 1, the primary amine and the tertiary amine together containing only one sulphonic acid group.

6. A method as claimed in claim 5 wherein the primary amine is 2-amino-1,3-benzthiazole-5-sulphonic acid.

7. A method as claimed in claim 5 conducted substantially as hereinbefore described with reference to any one of the foregoing Examples.

8. A water-soluble monoazo dye whenever prepared by a method claimed in any one of claims 5 to 7.

9. A process for the coloration of polyamide textile materials which comprises applying thereto a water-soluble monoazo dye as claimed in any one of claims 1 to 4 and 8.

10. Polyamide textile materials whenever coloured by the process claimed in claim 9.

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